

## Electro - chemical Fluid Splitting Using a Nanocomposite of NiO-NiFe<sub>2</sub>O<sub>4</sub>/MWCNTs as an Electrocatalyst

**Halesh Koti<sup>1\*</sup>, A Vijaya Krishna<sup>1</sup>, S.C.Sireesha<sup>1</sup>**

<sup>1</sup>*Department of Mechanical Engineering, Malla Reddy Engineering College, Telangana 500100, India*

*\*Corresponding Author Email: halkoti@gmail.com*

### Abstract

The key to fuel production through water splitting is escalating energy demands, scarcity of conventional energy resources, and environmental concerns. Various electrocatalysts have been reported, with cost effectiveness, stability, and OER (oxygen evolution reaction) activity being the most important factors. In the same vein, the current study looked into porous hybrid NiO-NiFe<sub>2</sub>O<sub>4</sub>/MWCNTs nanocomposite as an OER electrocatalyst. Tween was used as a surfactant in the synthesis, which was accomplished through co-precipitation. Using appropriate tools, a characterization and electrochemical study for water electrolysis was carried out using a synthesised electrocatalyst deposited glassy Carbon (GC) electrode as anode. Iron-doped Nickel oxide nanoparticles were created, recognising NiO's excellent oxygen evolution activity and its increased conductivity with Fe incorporation due to its higher electropositivity. Nanocomposites were created by incorporating up to 20% weight percent MWCNT (Multiwall carbon nanotubes). MWCNTs' high surface-to-volume ratios, stability, and excellent conductivity, as well as the reduction in crystallite size due to their incorporation, significantly improved the electrocatalyst's performance. The formation of NiO and NiFe<sub>2</sub>O<sub>4</sub> hybrids at a specific calcination temperature was also discovered to be the cause of increased OER activity due to increased grain boundaries. In alkaline media, porous NiO-NiFe<sub>2</sub>O<sub>4</sub>/MWCNTs with a 10% MWCNT concentration outperformed with a current density of 35mA/cm<sup>2</sup> at 1.8V.

### Introduction

Energy is essential to any country's economy; however, growing environmental concerns are driving a greater search for renewable and clean energy resources. One of the dependable sources for addressing such concerns has been identified as fuel production via water splitting. Water is a cheap and environmentally friendly source of hydrogen. Because of its light weight, high energy density, high storage capabilities, and environmental friendliness, hydrogen is regarded as a promising fuel. During the water splitting reaction, hydrogen evolution is relatively simple; however, oxygen evolution requires anode catalyst manipulation to achieve a lower activation potential. Because OER (Oxygen evolution reaction) occurs in multiple steps, each of which requires electrons, they have a wide activation potential barrier. The slow OER is due to the high activation energy for electron transfer, and thus the search for an efficient OER catalyst is of great interest[1].

Because of their higher electrical conductivity, atomic diffusivity, oxygen ion mobility, and catalytic activity, metal oxides are regarded as one of the most important candidates in the WOCs (Water oxidation catalysts) family. Their high catalytic activity is attributed to the presence of various defects such as vacant lattice sites, electron-hole pairs, interstitial sites, dislocations, and impurities, among others. [2-3]. Ir, Ru, IrO<sub>2</sub>, and RuO<sub>2</sub> are the most well-known catalysts for both acidic and basic media. [4-5] However, due to scarcity and high costs, their industrial application for water electrolysis is limited [6]. IrOx/SrIrO<sub>3</sub>, Cu<sub>2</sub>O, Cu<sub>2</sub>O/ITO, IrxO/ATO, and TiO<sub>2</sub>/CuO have also received a lot of attention [7-9]. Some metallic catalysts have been found to form stable oxide layers, resulting in good electrolytic activities; however, not all metallic catalysts are suitable. For example, Ru exhibits significant OER when used in metallic form rather than oxide form; however, the oxide layer formed on its surface is unstable and dissolving during reaction .

CoFe<sub>2</sub>O<sub>3</sub>, NiCo<sub>2</sub>O<sub>4</sub>, MnCo<sub>2</sub>O<sub>4</sub>, CuCo<sub>2</sub>O<sub>4</sub> and ZnCoO<sub>4</sub> are some of the other noticeably good electro-catalysts. The reason for their good performance has been attributed to the non-uniform charge distribution, thereby, generating active sites. High conductivity is also desirable along with active sites which can be achieved by doping with high conductivity metals. Intrinsic conductivity of active metals (e.g Ni, Fe, Mn, Co etc.) makes them attractive candidates for OER. They usually form oxide layers on their surface during OER mechanism. One of the pitfalls of spontaneous formation of oxide layer on their surface is uncontrolled composition of their lattice structure but still their fresh growth is advantageous for aging issues. Ni having oxidation state +2 (in NiO) which is compatible with the oxidation state for OER and is considered the most active catalyst, however, has relatively inferior crystallinity; it can be improved by incorporation of conductive metals. Although smaller particle size leads to greater surface area resulting in improved activity, however, crystallinity and conductivity are compromised. Therefore, for the optimization of activity and conductivity simultaneously, incorporation of Fe, Mo and Co have been proved to be better for electrolysis compared with pure NiO and its alloys. However, iron has demonstrated higher efficiency . reported the synthesis of Fe<sub>x</sub>Ni<sub>1-x</sub>O nanoparticles with doping concentration of Fe up to 20% and observed decrease in particle size with increasing concentration of iron. 10% Fe doped particles showed superior OER efficiency and turn over frequency even higher than

IrO catalyst in basic media. Similarly, reported a study of intentional and unintentional electrochemical incorporation of Fe in Nickel hydroxide and oxy-hydroxide films; Fe inclusions showed almost 30-fold improved activity in basic media. Fe incorporation is believed to provide abundance of Ni<sup>+3</sup>/Ni<sup>+4</sup> and Ni vacancies due to its higher electronegativity resulting in increased efficiency.

Zhang et al reported the fabrication of Ni/NiO on a carbon fiber paper, with good stability in basic media. Louie et al also reported Ni, Fe and Fe-Ni based electro-catalytic films fabricated via electro-deposition over gold electrodes. Ni-Fe films with 40% of iron content showed 3 and 2 folds higher OER efficiency comparing to pure Fe and Ni films, respectively. Song et al reported synthesis of Iron-Nickel electro-catalyst and claimed the outperformance of the synthesized catalyst over all the other existing reported Iron-Nickel oxide catalysts. Catalyst was electrochemically deposited over Ni Foam, Au and GC (Glassy Carbon) substrates for comparison; all substrates types showed near equal performance.

Carbon based compounds also have been studied for electrolysis. Although due to highly ordered lattice sp<sup>2</sup> hybrid structures, OER overpotentials of carbons are significantly higher, however, their low costs, good conductivity, high surface area and design versatility makes them attractive for electro-catalytic applications. Greater activation sites are required for better OER; it can be generated by manipulating hexagonal sp<sup>2</sup> network by functionalization, for example, by acid treatment. Gong et al reported the synthesis of Ni/NiO nano-composite with CNTs via hydrolysis. Ni/CNT, NiO/CNT and CNT alone showed inferior HER performance compared with NiO/Ni-CNT composite. Outperformance of NiO/Ni-CNT composite is credited to its higher surface area and collaboration of NiO and Ni.

NiO and Fe-doped Nickel oxides have been considered excellent and most suitable candidates as electrocatalysts for electrochemical water splitting. Although incorporation of CNTs in Nickel oxides has been reported, however, porous NiO-NiFe<sub>2</sub>O<sub>4</sub> hybrid with MWCNTs has not been well-attempted. This paper discusses a facile composition of porous hybrid NiO-NiFe<sub>2</sub>O<sub>4</sub>/MWCNTs electrocatalyst for electrochemical water splitting in alkaline media; the electrocatalyst has been found suitable for mass production along with its low cost and stability.

## Experimentation

### Chemicals

Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>99.0%, Sigma Aldrich), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (>99.0%, Sigma Aldrich), acetone (>99.8%, VWR Chemicals), ethanol (>99.9%, Labscan Asia Co. Ltd), MWCNTs (>90%, Sun Nanotek Co. Ltd.), Tween 85 (Sigma Aldrich), Nafion (Sigma Aldrich).

**Synthesis of NiFe<sub>2</sub>O<sub>4</sub> Nanoparticles without Tween** Iron Nickel Oxide nanoparticles were synthesized by coprecipitation method. Iron to Nickel ratio was kept as 15:85. Solution of 1M NaOH in 50ml deionized water was prepared by pouring 2mg of NaOH in 50ml of DI (deionized) water, under stirring at a temperature of 60°C and was named as Solution-1.

Another 2.5M solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 20ml of DI water was prepared by adding 3mg and 12.35mg of iron nitrate and nickel nitrate, respectively; this solution designated as Solution-2, was stirred well enough for 1 hour. Afterwards, Solution-2 was drop-wise added in Solution-1 maintained at 60°C; the stirring continued for 4 hours at the same temperature. Later, washing was done by centrifugation at 3500rpm for 15 min at ambient temperature.

Sample was thoroughly washed two times with DI water, one time with acetone and again twice with DI water. The collected samples were dried at 60°C overnight in oven and later were calcinated at different temperatures (between 500°C and 800°C) for 3 hrs in a muffle furnace, for comparison.

### Synthesis of NiFe<sub>2</sub>O<sub>4</sub> Nanoparticles with Tween

Iron Nickel Oxide NPs (nanoparticles) were prepared by the same procedure as discussed in the previous section, however, with the addition of surfactant (Tween 85). 10ml of the Tween was added in 1M NaOH solution in 50ml DI water at 60°C with vigorous stirring. Solution-2 was prepared in the same manner and after drop wise addition in Solution-1 maintained at 60°C in oven for 4 hrs. Afterwards, washing via centrifugation, drying and calcination at different temperatures were also performed as per previously mentioned scheme.

### Functionalization of MWCNTs

MWCNTs were functionalized using acidic approach. 0.65g of the CNTs were added into 15ml mixture of concentrated acid HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (1/3 v/v) and was sonicated for half an hour. In an oil bath with temperature of 90°C, the dispersed mixture was suspended and was refluxed for 7.5 hours under continuous stirring. Acid treatment was used for introducing eCOOH on the walls of MWCNTs, which was expected not only to enhance chemical reactivity but also to remove residual impurities [29]. Elimination of residual impurities resulted in reduction of charge carrier inhomogeneity leading to better charge mobility thereby enhancing electrochemical properties of the catalyst. Neutralization of the MWCNTs was then performed by centrifugation several times with DI water until neutral pH was obtained, followed by drying at 70°C in a vacuum oven.

### Formation of NiO-NiFe<sub>2</sub>O<sub>4</sub>/functionalized MWCNTs Nanocomposites

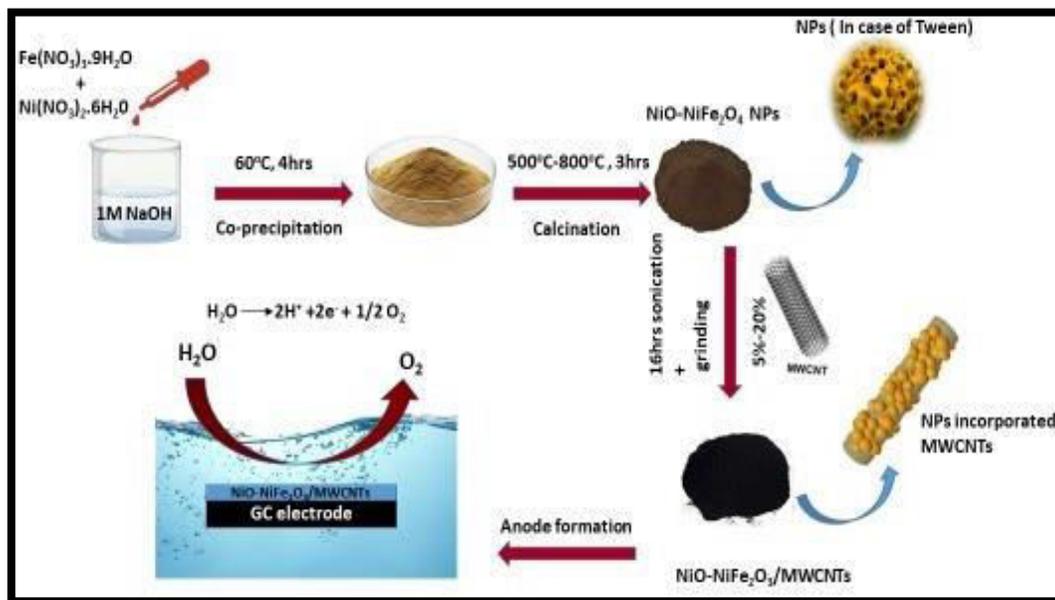
Composites of synthesized Nickel iron oxide NPs (both with and without surfactant) with various proportions of functionalized CNTs (5%, 10%, 15% and 20%) were prepared by making dispersion in orthoxylene. For each composite NPs and MWCNTs were both poured separately in specific proportions in 10ml orthoxylene and sonicated (SONREX Digit DT52 H, BANDELIN, Germany 240 Watts, 35kHz) for

1.5hr. Afterward these were mixed dropwise and sonicated at ambient temperature for 16 hours for thorough dispersion, followed by drying at 60°C overnight in oven and grinding using mortar & pestle for more than an hour, resulting in nanocomposites. The same procedure was followed for fabrication of all composites using mentioned proportions of the ingredients.

**Preparation of Anode**

For preparation of anode 2mg of the sample was poured into

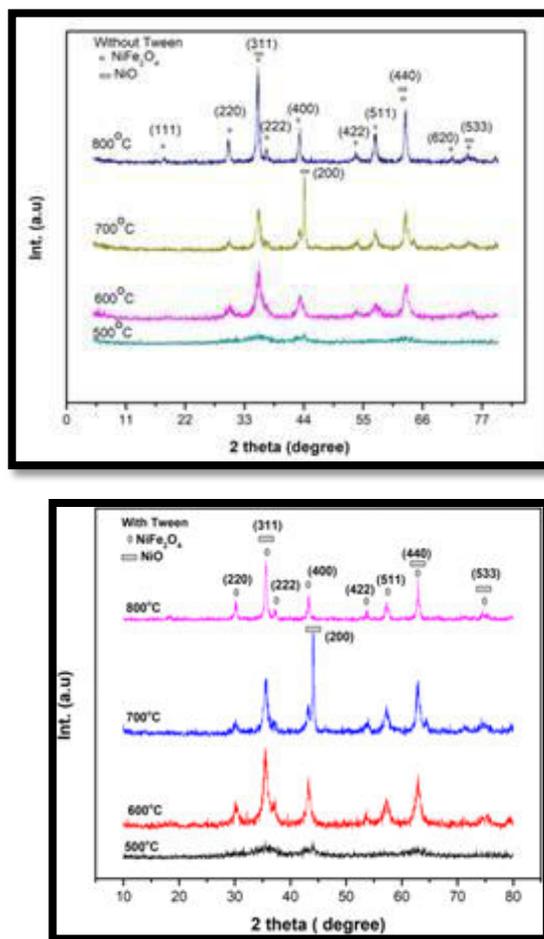
1ml solution of DI water and ethanol in a ratio of 2:1, respectively. For 2:1 solution of DI: ethanol, 320 µl of the ethanol was poured into 680µl of deionized water (DI). 30µl of Nafion was also poured as a binder. The solution was then sonicated for 1hr in a bath sonicator. With the help of micropipette 5µl of the mixture was then drop-cast on a cleaned GC (glassy Carbon) electrode. The electrode was then left overnight for drying at ambient temperature.



**Figure 2: Schematic diagram of NiO-NiFe<sub>2</sub>O<sub>4</sub>/f-MWCNT synthesis**

**Results and Discussion**

Structure confirmation and investigation of crystallographic properties of the synthesized catalysts was conducted by XRD (STOE-Seifert X'pert PRO), using CuK $\alpha$  radiations ( $\lambda=0.154\text{nm}$ ). Fig. 2(a) exhibits XRD graph of the NiO-NiFe<sub>2</sub>O<sub>4</sub> Nanoparticles synthesized without surfactant, calcinated at various temperatures for 3hrs. Absence of well-defined peaks for particles calcinated below 600°C, depicted that the formation of the phase started at 600°C and below this temperature the structure was amorphous with no crystalline phase. Diffraction peaks at  $2\theta=18^\circ$  (111),  $30^\circ$  (220),  $35.4^\circ$  (311),  $37^\circ$  (222),  $43^\circ$  (400),  $53.5^\circ$  (422),  $57^\circ$  (511),  $62.7^\circ$  (440),  $70.7^\circ$  (620),  $73.9^\circ$  (533) and  $79^\circ$  (444) confirmed the formation of cubic structure of NiFe<sub>2</sub>O<sub>4</sub> with JCPDS Card No. 01-088-0380. Whereas peaks around  $37^\circ$  (111),  $43^\circ$  (200),  $62.7^\circ$  (220) and  $79^\circ$  (222) confirms the formation of NiO phase with JCPDS Card No 847-1049. No extra peaks were obtained depicting the absence of any significant amount of any kind of impurity. Furthermore, it was observed that the peak intensity was increased with increasing temperature from bottom to top, whereas, and the width decreased; this could be attributed to the increasing crystallite size with increase in temperature [30]. Another factor to be considered here was that at 800°C NiO phase (which is more dominant at 700°C) had vanished. This might also have contributed to the increase of crystallite size, since hybrids and doping had been acknowledged to cause reduction of crystallite size [31-33]. Fig. 2(b) exhibits the XRD graph of Nickel Iron Oxides synthesized using a surfactant (Tween); peaks at  $2\theta=18^\circ$  (111),  $30^\circ$  (220),  $35.4^\circ$  (311),  $37^\circ$  (222),  $43^\circ$  (400),  $53.5^\circ$  (422),  $57^\circ$  (511),  $62.7^\circ$  (440),  $70.7^\circ$  (620),  $73.9^\circ$  (533) and  $79^\circ$  (444) were recognized. The obtained peaks with specific dhkl planes assured the formation of cubic structure of NiFe<sub>2</sub>O<sub>4</sub> (JCPDS Card no. 01-088-0380).



**Figure 2: (a) XRD patterns of NiFe<sub>2</sub>O<sub>4</sub> (a) synthesized without Tween (b) synthesized with Tween**

Neither extra peaks were found nor any peak shift was observed, indicating the absence of any significant impurity. Whereas peaks around 37° (111), 43° (200), 62.7° (220) and 79° (222) confirmed the formation of NiO phase with JCPDS Card no 847-1049. Like NPs without surfactant, the peak intensity and width for NPs with surfactant followed a similar trend and exhibited no NiO peak at 800°C. The XRD patterns for the both cases (i.e. with and without Tween) appeared similar.

Fig.3 manifests a comparison of XRD patterns of pure NiO-NiFe<sub>2</sub>O<sub>4</sub> and NiO-NiFe<sub>2</sub>O<sub>4</sub>/MWCNTs (various percentages). Diffraction peaks at 2θ = 18° (111), 30° (220), 35.4° (311), 37° (222), 43° (400), 53.5° (422), 57° (511), 62.7° (440), 70.7° (620), 73.9° (533) and 79° (444) were obtained for pure NiO-NiFe<sub>2</sub>O<sub>4</sub> and NiO-NiFe<sub>2</sub>O<sub>4</sub>/MWCNTs composite. Only a small negligible peak was obtained at around 26° which could be attributed to uniform distribution and anchoring of NiO-NiFe<sub>2</sub>O<sub>4</sub> on CNTs. Another reason for this small peak could be attributed to the very small quantity of CNTs in comparison to NiO-NiFe<sub>2</sub>O<sub>4</sub> [34]. Also a small change in the FWHM (full width at half maximum) was observed. CNTs incorporation slightly increased FWHM which could be attributed to the introduction of impurity due to CNTs and reduction of crystallite size. [35] This comparison also indicated that no phase change occurred in case of formation of CNTs composite.

**Conclusions**

Co-precipitation was used to create NiO-NiFe<sub>2</sub>O<sub>4</sub>/MWCNTs nanocomposites with and without surfactant. After that, electrochemical studies for water splitting were carried out using electrodes made from synthesised nanocomposites. The NiO-NiFe<sub>2</sub>O<sub>4</sub> hybrid phase of NPs formed during calcination at 700°C in the presence of surfactant proved to be superior to other synthesised NPs and was thus chosen for composites formation. At 1.8V, a composite with an optimised 10% weight fraction of MWCNTs outperformed with a current density of 35mA/cm<sup>2</sup>. The results demonstrated that the prepared NiO-NiFe<sub>2</sub>O<sub>4</sub>/MWCNTs nanocomposites are a promising electro-catalyst for water electrolysis.

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